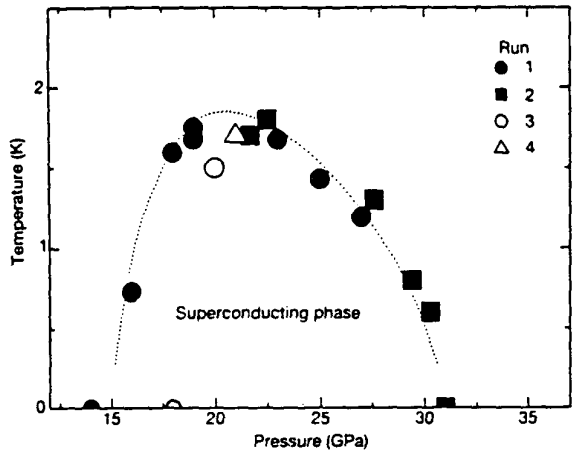

Figure 4 Superconducting phase diagram of iron. The transition temperature, $_c$, is defined by the onset of the transition. The dashed curve is a guide for the eye. $_c$ values shown by black circles and squares (runs 1 and 2) are obtained from electrical resistance measurements with sodium chloride as a pressure medium. Run 3 (white circle) is a run without a pressure medium while releasing the pressure from 90 GPa. Run 4 (white triangle) shows the onset of the Meissner signal in the magnetization measurement. $_c$ appears at around 15 GPa and increases with pressure. $_c$ reaches the maximum value of 2 K at around 21 GPa and vanishes above 30 GPa.

of the total residual resistivity. This is because the residual resistivity includes contributions from the thin gold wire in series with the sample as well as from the finite contact resistance, which is estimated to be around 90% of the measured resistance. The main impurities contained in the starting material were O, Ta, Si and Co at concentrations of 115, 10, 8.3 and 8.3 p.p.m., respectively, according to the chemical analysis data. Thus we regard the drop as the onset of superconductivity of iron.

To confirm the superconductivity, we tried to detect the Meissner effect using a SQUID (superconducting quantum interference device) magnetometer at 21 GPa. A 4:1 mixture of methanol/ethanol was used as the pressure-transmitting medium. An iron sample was obtained from the rod that provided the samples used for the resistance measurements, cut into slices 0.04 mm in thickness and 0.15 mm in diameter, and placed in the chamber of the BeCu gasket. Several turns of pick-up coil for the SQUID magnetometer were wound closely around the pressure surface of the diamond and an equal number of turns near to the diamond for background compensation. A small tin chip was put inside the compensation coil as a reference sample to check both the sign and the magnitude of the signal from iron. Figure 3 shows the superconducting transition signals from iron at 1.7 K and tin at 2.7 K, of opposite sign.

The pressure dependence of the transition temperature T_c was observed in the pressure range between 15 GPa and 30 GPa (Fig. 4). Superconductivity was observed in three different runs of the resistivity measurements and the magnetization measurement. Runs 1 and 2 were obtained by quasi-hydrostatic conditions with NaCl as the pressure-medium. No pressure-medium was used for run 3 and the superconductivity transition was observed only while reducing the pressure from 90 GPa. This implies that even a very small amount of remaining ferromagnetic b.c.c. iron may suppress the onset of superconductivity and that its transformation to h.c.p. iron is caused by either quasi-hydrostatic pressure or by increasing the pressure as much as possible. We conclude that the superconducting phase of iron appears after the establishment of the non-magnetic state at 15 GPa, which is close to the beginning of the b.c.c.-to-h.c.p. structural transition of iron. □

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Direct observation of hole transfer through DNA by hopping between adenine bases and by tunnelling

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The function of DNA during oxidative stress[1] and its suitability as a potential building block for molecular devices[2–4] depend on long-distance transfer of electrons and holes through the molecule, yet many conflicting measurements of the efficiency of this process have been reported[5,6]. It is accepted that charges are transported over long distances through a multistep hopping reaction[7–11]; this 'G-hopping'[8] involves positive charges moving between guanines (Gs), the DNA bases with the lowest ionization potential. But the mechanism fails to explain the persistence of efficient charge transfer when the guanine sites are distant[7,12], where transfer rates do not, as expected, decrease rapidly with transfer distance. Here we show experimentally that the rate of charge transfer between two guanine bases decreases with increasing separation only if the guanines are separated by no more than three base pairs; if more bridging base pairs are present, the transfer rates exhibit only a weak distance dependence. We attribute this distinct change in the distance dependence of the rate of charge transfer through DNA to a shift from coherent superexchange charge transfer (tunnelling) at short distances to a process mediated by thermally induced hopping of charges between adenine bases (A-hopping) at long distances. Our results confirm theoretical predictions of this behaviour[13–17], emphasizing that seemingly contradictory observations of a strong[8,9] as well as a weak[7,12] influence of distance on DNA charge transfer are readily explained by a change in the transfer mechanism.

We have measured the efficiency of the charge transfer between Gs, separated by adenine-thymine (A·T)$_n$ bridges of various lengths, in double strands **1a–h** (Fig. 1). Photolysis of the 4′-acylated nucleotide in DNA **1** generates the sugar radical cation in **2** (Fig. 1), which injects a positive charge into G_{22} of the complementary, radiolabelled strand (**2** → **3**; Fig. 1). This guanine radical cation G_{22}^{+} is either trapped irreversibly by water, yielding after piperidine treatment the strand cleavage product P_G, or it induces an electron

(hole) transfer through DNA (3 4; Fig. 1). In order to build up a driving force for the charge transfer process, we used as electron donor a GGG triplet that is more easily oxidized than a single G[18]. The positive charge reaching the GGG unit was quantified by the water trapping product P_{GGG}, and the yield ratios P_{GGG}/P_G were determined by gel electrophoresis. We observed the product ratios shown in Fig. 2; to obtain these results, we used the assay of ref. 19 but changed the pH from 7.0 to 5.0.

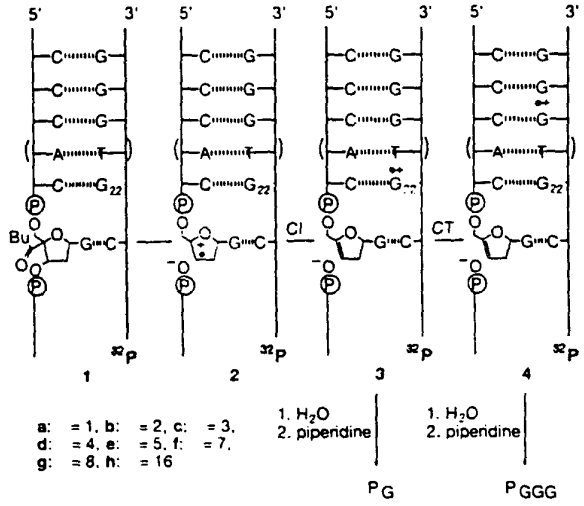

Figure 1 Charge injection and charge transfer in DNA strands. Illustrated are the method of charge injection (CI) into G_{22} (2 3) and charge transfer (CT) to the GGG sequence (3 4), starting from DNA strands **1a–h** that contain a 4 -acylated deoxyguanoside (in red). The double strands above and below the depicted sequences are identical to those used in earlier studies[19]. Photolyses of **1a–h** were performed at pH 5.0 (citrate buffer) with a 500-W, high-pressure Hg lamp (320 nm cut-off filter) in the absence of oxygen at 15 C. Trapping by water of the charge at G_{22} and GGG leads to cleavage products P_G and P_{GGG}, respectively, after piperidine treatment. The nucleotides in red indicate the charge precursor (**1**), the injection site (**2**), the charge donor (**3**), and the charge acceptor (**4**).

The data in Fig. 2 show that the efficiency of the charge transfer, measured by the P_{GGG}/P_G ratio, drops by a factor of 8 for each additional A T base pair in short $(A T)_n$ bridges (n = 1–3). But in longer sequences (n = 4–7), the P_{GGG}/P_G ratio decreases only very slightly when the number of A T base pairs increases (Fig. 2). At further elongation of the $(A T)_n$ sequence, the distance influence vanishes completely. Thus, we observed no change in the P_{GGG}/P_G ratio by increasing the number of A T base pairs from n = 7 to n = 16. A plot of log P_{GGG}/P_G against the number n of the A T base pairs between the guanines exhibits a clear switch of the influence of distance on the charge transfer (Fig. 3).

Such a distance dependence, which demonstrates a change of the reaction mechanism, has been predicted recently[13–17]. From being a coherent superexchange charge transfer (tunnelling) process at short distances, the mechanism becomes a thermally induced hopping process for long $(A T)_n$ sequences, where the adenines are involved as charge carriers (A-hopping)[17]. A switch between these reaction mechanisms occurs because tunnelling rates decrease considerably as the distance increases (see the steep line at low n in Fig. 3)[8,9]. Therefore, in DNA strands where the guanines are separated from each other by long $(A T)_n$ sequences, endothermic[20] transfer of the positive charge from a guanine radical cation (G^+) to an adjacent adenine becomes faster than the direct transfer of this charge to the distant guanine. The subsequent migration of the positive charge between the adenines (A-hopping) is so rapid that the length of the $(A T)_n$ sequence plays only a minor role. Further experiments with DNA double strands 5 and 6 show that, in contrast to the behaviour seen with guanine radical cations, trapping of adenine radical cations by water is insignificant (Fig. 4). This difference is expected[17], because the water trapping reaction of adenine radical cations proceeds through a transition state, which is much higher in energy than the transition state associated with

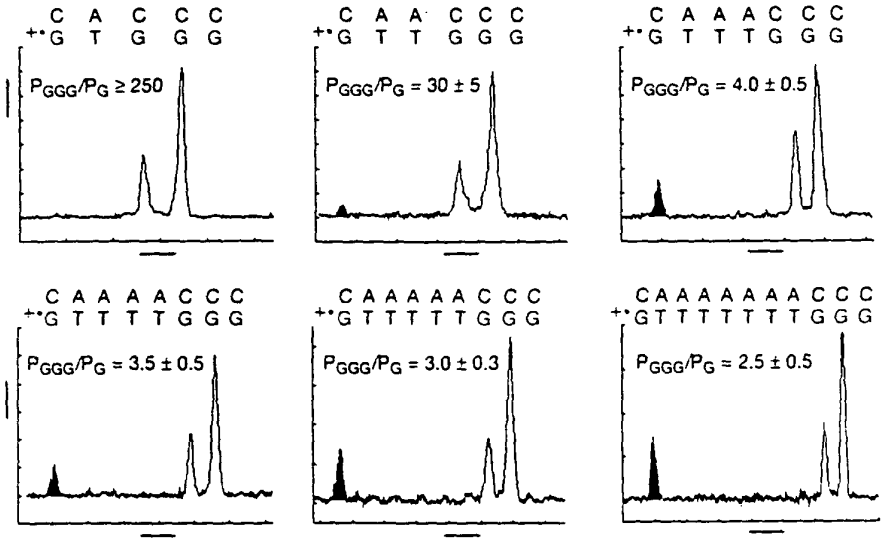

Figure 2 Ratios of the irradiation products derived from initially formed guanine radical cations to those derived after charge transfer across (A T) bridges. The individual curves show radioactivity intensities of radiolabelled DNA strands subjected to gel electrophoresis using denaturing polyacrylamide gels. They are obtained by subtraction of intensities measured in control experiments (irradiation of unmodified strands) from intensities measured in irradiation experiments with the modified strands **1a–h**. The peaks in intensity ( ) correspond to products P_G (shown in red) and P_{GGG}. The peak areas are relative yields, thus the P_{GGG}/P_G ratios are yield ratios. The products are formed by water trapping of the guanine radical cations G^+ and subsequent site-selective strand cleavage of the radiolabelled strand. Each peak arises at the nucleotide position ( ) shown in the strand depicted at the top of each panel. The nucleotides in red indicate the beginning and the end of the charge transfer process.

the trapping reaction of the guanine radical cation. The data of Fig. 4 also confirm[17] that interstrand A-hopping steps lead to a slight decrease of the hole transfer efficiency.

Our experiments show the presence of two different processes for the hole transfer between guanines in DNA: (1) a coherent superexchange reaction (single-step tunnelling), where the bridging adenines are indirectly affecting the transfer mechanism by mediating the electronic coupling between the guanines, and (2) a thermally induced hopping process (A-hopping mechanism), where the lifetime of the guanine radical cation is long enough to oxidize the intervening adenine bases and directly involve them in charge transport. The efficiency of the tunnelling reaction decreases rapidly with the number of the intervening A T base pairs, whereas the A-hopping process is only slightly influenced by the number of the A T base pairs. Thus, the debated contradiction between very strong[8,9] and very weak[7,12] influence of distance on the hole transfer through DNA can be explained by a change in the reaction mechanism.

These results indicate that A-hopping provides a mechanism for ameliorating the harmfulness of damage to DNA under conditions of oxidative stress, by providing a means for charge transport over long sequences of A T pairs into regions of low ionization potentials[1,21]. In addition, the ability to rationally change the behaviour of a system from strongly distance-dependent charge transfer to weakly distance-dependent charge transfer may open new opportunities in nanoelectronics. DNA can offer this ability because the switch to the activated hopping mechanism depends on the difference of the oxidation potentials of the DNA bases involved—and this difference could be easily changed by using suitable substituents. □

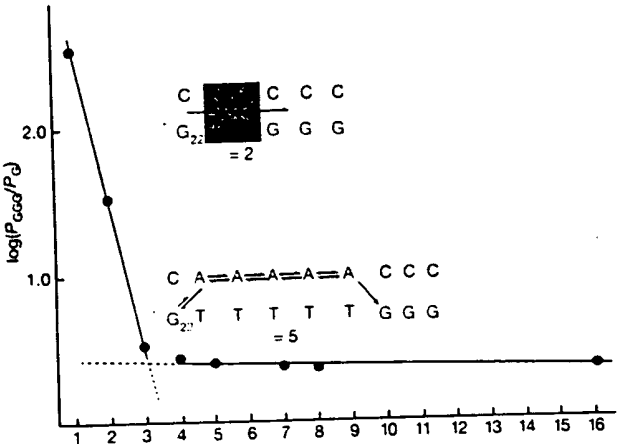

Figure 3 Plot of $\log(P_{GGG}/P_G)$ against the number of the A T base pairs. Each experiment was performed three times, and their relative errors are within 10–20% (see Fig. 2). The steep line corresponds to the coherent superexchange charge transfer. Its slope leads to ($\beta = 0.6$ Å $^{-1}$) of the Marcus-Levich-Jortner equation[10]. The flat line is drawn in order to make clear the weak distance dependence. The product ratios P_{GGG}/P_G are proportional to the charge transfer rates. The arrows in the depicted DNA strands indicate the superexchange charge transfer between G_{22}^+ and the GGG sequence for short distances (= 2), or the A-hopping mechanism for long distances (= 5), where—in addition—adenines act as charge carriers. For clarity, only the double strands with = 2 and = 5 are shown. The nucleotides in red indicate all charge carriers.

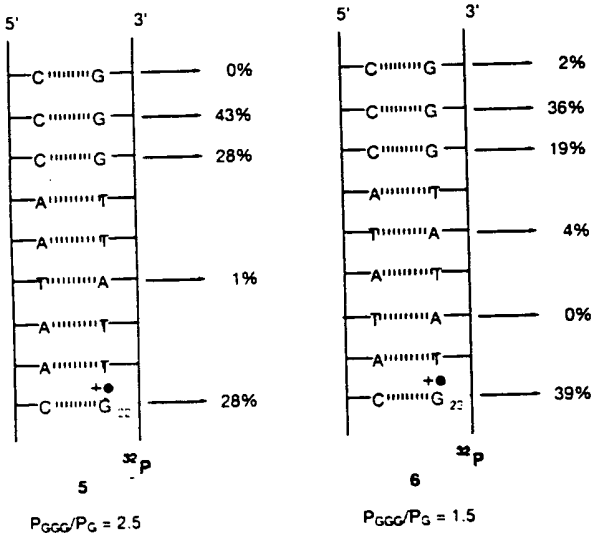

Figure 4 Relative yields of water trapping products during hole transfer through DNA sequences **5** and **6**. The experiments were performed three times (strand **5**) or twice (strand **6**). The relative errors of yields of products P_{GGG} and P_G are 15%. The yields obtained by trapping the A sites have absolute errors of 4%. Trapping products of thymine bases could not be detected. The nucleotides in red indicate the beginning and the end of the charge transfer process.

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